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(wrong)**DERWENT-ACC-NO:** 1971-67455S**DERWENT-WEEK:** 197142

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TITLE: Nickel oxide rhenium contg reforming catalyst**PATENT-ASSIGNEE:** DU PONT DE NEMOURS & CO E I[DUPO]**PRIORITY-** 1971US-0119817 (March 1, 1971) , 1970US-0030258 (April
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INT-CL (IPC): C10G000/00**ABSTRACTED-PUB-NO:** BE 765482A**BASIC-ABSTRACT:**

Nickel oxide rhenium contg reforming catalyst This consists of nickel oxide combined with 0.01-20 % wt rhenium, the quantity of nickel being 5-10000 times that of the rhenium supported on a refractory oxide melting >1500 degrees C.

It is resistant to the deposition of carbon and to disintegration due to carbon, halides or sulphur, and to attrition.

The catalyst has a long life and a high reforming activity.

TITLE-TERMS: NICKEL OXIDE RHENIUM CONTAIN REFORM CATALYST**DERWENT-CLASS:** E31 H04 J04**CPI-CODES:** E35-T; E35-W; H04-F01; J04-A02;**CHEMICAL-** Chemical Indexing M3 *01* Fragmentation Code A428 A940
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(54) PROCESS FOR REFORMING HYDROCARBONS

(71) We, E.I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for catalytically reforming hydrocarbons.

Catalytic steam-hydrocarbon reforming is the major method employed by industry for producing hydrogen and synthesis gas mixtures. In this method gaseous hydrocarbons, such as methane and ethane, or hydrocarbons which may be vaporized at moderate temperatures, such as propane, butane and normally liquid hydrocarbons up to and including octane, are reacted with steam over a nickel catalyst at 650-1000°C. to produce carbon oxides and hydrogen. The primary reaction products are then processed further in various ways, depending on the final use for the hydrogen and on the purity required.

Thus when the hydrogen is used for ammonia synthesis gas production, air is added in a secondary reforming step over a nickel catalyst where the oxygen is consumed in partial oxidation and reforming of the residual unreacted hydrocarbons. The nitrogen in the air provides the nitrogen required in the ammonia synthesis gas. For methanol synthesis gas, the primary reaction product is cooled and carbon dioxide may or may not be removed to produce the mixture required. For high-purity hydrogen, the primary reaction product is reacted catalytically with additional steam to oxidize carbon monoxide to carbon dioxide. The carbon dioxide is then removed and finally the residual carbon monoxide is hydrogenated to methane to produce high-purity hydrogen.

drogenated to methane to produce high-purity hydrogen.

The catalysts which are commercially available for use in manufacturing plants using the steam-hydrocarbon reforming process generally contain 10 to 50 weight % nickel oxide mixed with a refractory, usually alumina, and a cement or binder such as calcium aluminate. The catalyst is generally pelleted into cylinders 0.5, 0.625 or 0.75 in. in diameter and length or formed into Raschig rings of similar size. These pellets or rings are placed in tubes located in a heating furnace. The hydrocarbon stream and steam are then passed through the heated tubes to produce hydrogen and carbon oxides.

While in use, the catalysts presently used are subject to loss of activity and disintegration resulting in unacceptable pressure drop caused by the plugging of the catalyst tubes. Such catalyst failures are very costly since generally a long shutdown is necessary to remove and to recharge the catalyst.

We have discovered that if the conventional nickel oxide reforming catalyst is modified by the addition thereto and 0.01% to 20.0% by weight of rhenium, based on the nickel present in the catalyst, an improved catalyst is obtained. The catalyst resists carbon deposition and disintegration due to carbon, halides or sulfur under operating conditions which cause substantial disintegration of conventional nickel oxide catalysts. The rhenium-modified catalyst also appears to have improved resistance to spalling of the active components. The catalysts of the invention also provide improved catalytic activity in the reforming operation.

Accordingly the present invention provides a process for reforming hydrocarbons which comprises contacting a hydrocarbon feed with steam at a temperature of from 650°C to 1000°C. in the presence of a cata-

[Price 25p]

lyst which comprises nickel oxide in combination with from 0.01% to 20% by weight, based on the amount of nickel, of rhenium in either elemental or combined form.

The rhenium can be present in the rhenium-modified nickel oxide catalyst as elemental rhenium, rhenium oxide or the solid state reaction product of rhenium oxide with the other oxides present, e.g. nickel perrhenate and/or nickel rhenate.

The catalyst also can contain up to 100, preferably 5 to 25 parts by weight, per part by weight of nickel, of a stabiliser or promoter such as uranium oxide, chromium oxide, alumina, zirconium oxide, thorium oxide, barium oxide, silica, titania, strontium oxide, calcium oxide, magnesium oxide, manganese oxide, molybdenum oxide, tungsten oxide, niobium oxide, tantalum oxide, lathium oxide, cerium oxide, praseodymium oxide, other individual or mixed rare earth oxide(s) or nickel chromite.

Particularly preferred as a promoter is manganese oxide. This compound is a very useful co-promoter with the rhenium as it minimizes carbon deposition and it can replace a portion of the more expensive rhenium without loss in catalytic activity.

A preferred catalyst contains 0.1 to 10% by weight of manganese oxide and 0.05 to 5% by weight of rhenium, based on the total weight of the catalyst.

The catalyst can be unsupported but preferably is supported on a conventional catalyst support, i.e. any refractory oxide melting above 1500°C. or a suitable metal or alloy. Suitable supports include alumina, chromium oxide, mullite, spinel, silica, silica-alumina, thorium oxide, magnesia, stainless steel, steel, nickel and alloys of nickel with aluminium, thorium, chromium or iron.

If the catalyst is supported, the active material, i.e. the nickel oxide-rhenium-promoter or stabiliser combination, preferably should constitute from 0.1 to 25% by weight of the catalyst.

The catalyst can be made by conventional techniques. Thus the catalyst can be made by impregnating a refractory support with a solution containing the catalytic active ingredients and then calcining to activate. The temperature of calcining is not critical and can vary from 650°C to 1200°C. When the support is alumina the techniques used to prepare prior art nickel oxide-alumina catalysts may be utilised with the additional step of adding rhenium.

A supported catalyst can also be made by adding a cement to the catalytically active materials and cementing them to the support. Useful cements include Sorel cement, calcium aluminate, alumina gel and

colloidal alumina.

Alternatively, the catalyst can be made by co-precipitation of the catalytic components, with or without the support material. The co-precipitation is brought about by preparing a solution of the catalytic components and then adding a precipitating agent, e.g. ammonium carbonate, ammonia or ammonium oxalate, to the solution. The precipitate can be mixed with a suitable adhesive, e.g. nickel nitrate, colloidal silica sol, alumina gel or colloidal boehmite, and then pilled or extruded into the desired form. This form can vary widely but usually will be in the shape of rods, tubes or saddles.

Ceramic materials, such as alpha alumina, mullite, sillimanite and zirconia, are satisfactory as supports and can be obtained with various porosity, surface roughness, geometry, surface area and density to achieve optimum rigidity, internal activity and anchoring sites for the catalytic coating. Under certain high temperature and pressure conditions, silica and alkalis must be avoided, so this must be taken into account when selecting the support.

When a non-nickel metallic support is used in the manufacture of the catalyst, nickel must be applied to the surface of the support. This application can be accomplished by many methods and the particular technique used is not critical. For example, the metallic support can be etched with an acid, e.g. nitric acid or a mixture of nitric acid and acetic acid, or with bromine in methanol or with ferric chloride in ethanol. Any material which will etch the non-nickel surface to form a rough surface will suffice.

After the support surface has been roughened, the support is impregnated with a suitable source of nickel in solution. Usually the rhenium will also be applied to the surface at this time, although it can be applied subsequently. The solution may be prepared using a material, for example a nitrate, sulfate, formate or acetate, which will decompose to nickel oxide on heating. For example, an etched wire can be dipped and then fired at 400°C. for two hours and in a solution of nickel nitrate hexahydrate then redipped and fired at 800°C. for 1 to 2 hours. The concentration of nickel in the impregnating solution will usually be from one to three molar. Redipping and firing at 400°C. may be carried out as many times as necessary to obtain the desired amount of added nickel.

Other methods of applying the nickel can be used; thus it could be applied from compositions of nickel oxide and alkaline silicate as taught in U.S. Patent No. 3,460,523.

In an alternative embodiment, a pure nickel support can be etched with, for example, nitric acid, dilute nitric acid, a mix-

ture of nitric acid and acetic acid, bromine or ferric chloride to obtain a rough, oxide surface, usually 10 seconds to 10 minutes being required. The bromine may be used in methanol and the ferric chloride may be used in ethanol or water. The nickel support can then be coated with rhenium and optionally additional nickel in the manner set forth above for a non-nickel support and calcined. When the support is an etched nickel wire, the wire coated with rhenium or nickel and rhenium may be charged to a vessel, e.g. the reformer, where it is heated in air at 500 to 2000°F. for sufficient time to convert the surface nickel to nickel oxide. The time depends upon the temperature; thus 90 minutes is sufficient at 1900°F., while several hours will be required at the lower temperatures.

Suitable sources of nickel for making the catalyst are nickel oxide and soluble salts of nickel, e.g. nickel nitrate, nickel chloride, nickel sulfate, nickel acetate and nickel formate.

Suitable sources of rhenium for making the catalyst are rhenium oxide, perrhenic acid and salts such as KReO_4 , NH_4ReO_4 , NaReO_4 , ReCl_6 , ReOCl_4 and ReBr_6 . These compounds and other sources of rhenium are described in "Rhenium Chemicals, Their Properties and Applications", published by the Cleveland Refractory Metals Division of Chase Brass and Copper Co., 1969.

The promoter or stabiliser can be incorporated in the catalyst by conventional techniques, e.g. by impregnation using a soluble salt of the promoter or stabiliser. Thus the solution containing nickel and rhenium values also may include aluminium nitrate, uranium nitrate, lanthanum nitrate or thorium nitrate; alternatively a solution of a precursor of the promoter or stabiliser can be added to a nickel oxide-rhenium catalyst.

The process according to the invention is applicable to the reforming of hydrocarbons, particularly methane, natural gas and naphtha, in the presence of reduced amounts of steam. The operation of the reformers is well known to those skilled in the art. Accordingly, this process will not be described in detail.

The following Examples illustrate the invention.

EXAMPLE 1

1. A solution was prepared by dissolving 25 parts by weight of nickel nitrate hexahydrate and 1.3 parts by weight of perrhenic acid (1.0 part by weight of elemental Re) in 50 parts by weight of distilled water.
2. 200 parts by weight were weighed out of alpha-alumina in the form of $1/8'' \times 1/8''$ right cylinders having a surface area

of approximately $1 \text{ m}^2/\text{g.}$, an apparent density of 1.1 g./ml. , a total pore volume of 0.4 ml./g. and pore dimensions largely in the 0.5 to 10 micron diameter range.

3. The support obtained in Item 2 was heated to 80°C. in an evaporating dish or suitable open-mouth container. Then the solution obtained in Item 1 was poured over the support and evaporated to dryness at 110°C. with constant stirring.

4. The uniformly coated support was then placed in a closed cylindrical vessel with openings at each end to permit hydrogen admission at one end and its withdrawal at the other. Hydrogen was then passed through the vessel while the charged vessel was heated gradually over a period of 3 hours so that the temperature increased at a uniform rate until a final temperature of 500°C. was reached. Hydrogen flow was at a rate such that the stoichiometric requirement to reduce the HReO_4 to elemental Re passed through the vessel each 15 minutes. The temperature was maintained at 500°C. for 1 hour after reaching 500°C.

The catalyst thus produced was effective for reforming a steam-natural gas mixture having a volume ratio of 2 steam to 1 natural gas at temperatures of 650°C. to 1000°C. and at space velocities as high as 2000 reciprocal hours relative to the natural gas feed.

The catalyst was especially effective in avoiding carbon deposition even at low steam to natural gas volume ratios. Furthermore, when carbon was purposely deposited on the catalyst by eliminating the steam entirely, carbon deposition was only slight, disintegration was absent and the catalyst was quickly regenerated to its original activity by replacing the natural gas with steam for a brief period until no further carbon oxides appeared in the off-gas.

Instead of using 25 parts by weight of nickel nitrate hexahydrate in the preparation of the catalyst, 10-200 parts by weight of nickel nitrate hexahydrate may be used, the resulting catalysts exhibiting similar excellent performance for hydrocarbon steam reforming.

Instead of using 1.3 parts by weight of perrhenic acid in the preparation of the catalyst 0.10-10.0 parts by weight of perrhenic acid may be used, the nickel content being varied if necessary so as not to exceed the maximum permissible amount of Re relative to Ni.

Instead of using nickel nitrate in the preparation of the catalyst there can be used a stoichiometrically equivalent amount of nickel chloride, nickel sulfate, nickel acetate or nickel formate, for example. Furthermore, instead of using perrhenic acid in the preparation of the catalyst there can be

used a stoichiometrically equivalent amount of ammonium perrhenate, potassium or sodium perrhenate, rhenium oxychloride, rhenium hexachloride or other soluble salt.

- 5 There also can be added to Item 1 a stabilizer or promoter or precursor thereof such as manganese nitrate, ammonium tungstate, ammonium molybdate, tantalum tetrachloride, niobium tetrachloride, alu-
10 minum nitrate, thorium nitrate or magnesium nitrate, for example.

- Instead of using the cylindrically shaped alumina specified above, there can be used alumina in the form of saddles, rods, bars, honeycomb structure, rings, spheres or
15 hollow spheres. Furthermore, instead of alumina there can be used another refractory material such as mullite, zirconia, periclase, thoria, lanthana, ceria, chromia
20 or other refractory of high melting point.

EXAMPLE 2

1. A solution was prepared as described in Item 1 of Example 1.
25 2. Type 304 stainless steel wire having a diameter of 2 mils was formed into loosely compacted shapes resembling (scouring pad) pillows which were 1"×1"×1/2" thick. These pillows had an apparent density of
30 12 lbs./ft.³ when loosely packed.

3. The pillows were etched by exposure to a solution of aqua regia for a period of 10 minutes at 40°C.

4. The etched pillows were washed
35 thoroughly to remove chloride and then were dried and calcined in air at 400°C. for 2 hours.

5. The solution of Item 1 was coated onto the etched pillows to the extent that
40 an increase in weight of 3-5% was attained after calcining at 400°C.

- The catalyst thus produced was active for the reforming of natural gas and steam at temperatures of from 650° to 1000°C.
45 in a volume ratio of 1 natural gas to 2 steam.

- Instead of using aqua regia, etching can be performed by vapor phase reaction with elemental chlorine followed by washing or by treatment with a fused sodium hydroxide-sodium nitrate salt at 300°C. followed by
50 washing or by fusion with sodium peroxide at 200°C. The sodium peroxide should be diluted with sodium hydroxide to at least a 1:1 weight ratio to prevent excessive oxidation rate. Catalysts thus produced were
55 also effective for hydrocarbon steam reforming operations.

- Instead of natural gas, the hydrocarbon source can be propane, ethane, butane, naphtha or crude oil from various sources,
60 appropriate adjustment being made in respect of the proportion of steam to ensure a steam to hydrocarbon volume ratio of at least 1.5:1.

- 65 Instead of Type 304 stainless steel, there

can be used elemental nickel, Type 316 stainless steel, "Inconel", "Nichrome" and other alloys having refractory and corrosion resistant properties. ("Inconel" and "Nichrome" are Registered Trade Marks). 70

EXAMPLE 3

1. A solution was prepared by dissolving 25 parts by weight of nickel nitrate hexahydrate 0.3 parts by weight of perrhenic acid (equivalent to about 0.2 part by weight
75 of elemental rhenium) and 1.5 parts by weight of anhydrous manganese nitrate in 90 parts by weight of distilled water.

2. 200 parts by weight of α -alumina in
80 the form of 1/8"×1/8" right cylinders having a surface area and other physical characteristics similar to those specified in Item 2 of Example I were weighed out.

The catalyst was then prepared as per
85 Items 3 and 4 of Example I.

The catalyst produced was especially effective for the reforming of hydrocarbons in the presence of steam to produce synthesis gases rich in hydrogen, carbon monoxide and carbon dioxide. The catalyst thus
90 produced was also effective in averting carbonaceous deposition, particularly elemental carbon, on the catalyst surface, even when processing higher molecular weight hydrocarbons and operating at a low steam to
95 hydrocarbon volume ratio. For example, at 800°C, 15 lbs/sq. in. pressure and a 2:1 steam to hydrocarbon volume ratio, the efficiency of the reaction was such that more
100 than 97% of the hydrocarbon was converted at an hourly space velocity of 1500 on the basis of the product gas.

An effective catalyst can also be made by varying the perrhenic acid content from
105 as low as 0.05 parts by weight of rhenium to as high as 5 parts by weight rhenium. It is essential, however, that when low rhenium content is used, the manganese content be adjusted to a higher level to
110 compensate for the decreased quantity of rhenium. This adjustment is necessary to maintain the characteristics of the catalyst for minimum elemental carbon deposition.

The manganese content can be varied
115 from as low as 0.1 part by weight to as high as 10 parts by weight, keeping in mind that the manganese should always be present in sufficient quantity to compensate for a low rhenium level but should not be in
120 such a high quantity as to effect noticeable deactivation of the catalyst.

The catalysts described above can be used under elevated pressures up to and exceeding 500 psi provided that proper ad-
125 justment is made in respect of temperature, steam to hydrocarbon volume ratio or space velocity in order to achieve the desired conversion of the hydrocarbons to hydrogen, carbon monoxide and carbon dioxide. 130

WHAT WE CLAIM IS:—

1. A process for reforming hydrocarbons which comprises contacting a hydrocarbon feed with steam at a temperature of from 5 650°C to 1000°C. in the presence of a catalyst which comprises nickel oxide in combination with from 0.01% to 20% by weight, based on the amount of nickel, of rhenium in either elemental or combined form. 10
2. A process according to claim 1 wherein the nickel oxide and rhenium are supported on a carrier.
3. A process according to claim 2 wherein the carrier is a refractory metal oxide having melting temperature above 1500°C. 15
4. A process according to claim 2 wherein the carrier is alumina, chromium oxide, mullite, spinel, silica, silica-alumina, 20 thorium oxide, magnesia or zirconia.
5. A process according to any one of claims 1 to 4 wherein the catalyst also comprises up to 100 parts by weight, per part by weight of nickel, of a stabiliser or promoter. 25
6. A process according to claim 5, wherein the stabiliser or promoter is any compound specifically named herein as such.
7. A process according to either claim 5 30 or claim 6 wherein the stabiliser or promoter is present in an amount of from 5 to 25 parts by weight, per part by weight of nickel.
8. A process according to any one of the preceding claims wherein the nickel oxide, 35 rhenium and any stabiliser or promoter which may be present together constitute from 0.1% to 25% by weight of the catalyst.
9. A process according to any one of the preceding claims wherein the hydrocarbon 40 feed is methane.
10. A process according to claim 1 substantially as hereinbefore described.
11. The products of a reforming process 45 as claimed in any one of the preceding claims.
12. A process according to claim 1 wherein the catalyst comprises nickel oxide in combination with from 0.05 to 5% by weight 50 of rhenium and 0.1 to 10% by weight of, as promoter, manganese oxide based on the total weight of the catalyst.
13. The products of a reforming process 55 as claimed in claim 12.

J. A. KEMP & CO.,
Chartered Patent Agents,

14 South Square,
Gray's Inn,
London WC1R 5EU.

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